# Carbonate formation events in ALH 84001 trace the evolution of the Martian atmosphere

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**Carbonate minerals provide critical information for defining atmosphere–hydrosphere interactions. Carbonate minerals in the Martian meteorite ALH 84001 have been dated to ∼3.9 Ga, and both C and O-triple isotopes can be used to decipher the planet's climate history. Here we report $\Delta^{17}O$, $\delta^{18}O$, and $\delta^{13}C$ data of ALH 84001 of at least two varieties of carbonates, using a stepped acid dissolution technique paired with ion microprobe analyses to specifically target carbonates from distinct formation events and constrain the Martian atmosphere–hydrosphere–geosphere interactions and surficial aqueous alterations. These results indicate the presence of a Ca-rich carbonate phase enriched in $^{18}O$ that formed sometime after the primary aqueous event at 3.9 Ga. The phases showed excess $^{17}O$ (0.7‰) that captured the atmosphere–regolith chemical reservoir transfer, as well as $CO_2$, $O_3$, and $H_2O$ isotopic interactions at the time of formation of each specific carbonate. The carbon isotopes preserved in the Ca-rich carbonate phase indicate that the Noachian atmosphere of Mars was substantially depleted in $^{13}C$ compared with the modern atmosphere.**

Martian meteorite | oxygen isotope anomaly | aqueous interaction | carbon isotope | photochemistry

Geological evidence suggests that early Mars was sufficiently warm for liquid water to flow on the surface for at least brief periods, if not longer (1). Identifying the nature and duration of warmer conditions on the Martian surface is one of the key pieces of information for understanding atmosphere–hydrosphere–geosphere interactions, the evolution of the atmosphere, and potential past habitability. A better understanding of the evolution of the Martian atmosphere and, in particular, the behavior of its primary component, $CO_2$, provides a means for characterizing the nature of the ancient Martian environment. The amount of $CO_2$ present in the atmosphere should provide critical insight into the characteristics of the Martian climate, with a denser atmosphere being more likely to be able to support prolonged warmer temperatures (2, 3).

The Martian meteorite ALH 84001 is a critical source for understanding the history of the Martian atmosphere, as it is the oldest known rock (crystallographic age ∼4.09 ± 0.03 Ga) (4), and its carbonate fractions (<1% wt/wt) are considered to have preserved the carbon isotope signature of the ancient atmosphere ∼3.9 Ga ago (5). These carbonates are chemically (Mg-, Ca-, and Fe-Mn rich) and isotopically ($\delta^{13}C_{VPDB}$ = 27–64, where VPDB stands for Vienna Pee Dee Belemnite, and $\delta^{18}O_{SMOW}$ = −10–27‰, where SMOW stands for Standard Mean Ocean Water) heterogeneous on micrometer scales; carbon and oxygen isotopes show a covariant relationship that is correlated with Mg content of the mineral (6–8). The exact process responsible for their formation is not clear, although low-temperature aqueous precipitation, biogenic production, evaporation, and high-temperature reactions are all candidate processes (9–13). Decoding the fingerprints of various oxygen-carrying reservoirs on Mars (atmosphere–hydrosphere–geosphere) and how they interact from $\delta^{18}O$ alone is nearly impossible because of the lack of direct information on the isotopic composition of the primary O-carrying reservoirs in the carbonate system ($CO_2$–$H_2O$) and the extreme variability observed in chemical and isotopic composition of carbonate minerals in ALH 84001. The O-isotopic anomaly ($\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$) observed in $O_3$, $SO_4$, $NO_3$, $CO_3$, and $H_2O_2$ has been successfully used to investigate physicochemical and photochemical processes in terrestrial and extraterrestrial materials (14–18). In this study, we used five stable isotopes of carbonates ($^{12}C$, $^{13}C$, $^{16}O$, $^{17}O$, and $^{18}O$) on Ca- and Fe-rich phases to decipher atmosphere–hydrosphere interactions and Martian $CO_2/CO_3$ geochemical cycling. This high-precision multi-O-isotope analysis of secondary minerals was coordinated with detailed petrographic and ion microprobe analyses.

The primary goal of this study was to specifically identify carbonate phases from distinct formation events to provide better understanding of oxygen and carbon reservoirs on Mars. There have been no previous measurements of both carbon isotope and O-triple isotope compositions of the same $CO_2$ sample from ALH 84001, and previous measurements of O-triple isotopes did not attempt to use stepped extraction to separate different carbonate phases (19). To accomplish this goal, a stepped acid dissolution technique was performed to extract $CO_2$ from several portions of ALH 84001. The O-isotope values ($\Delta^{17}O$, $\delta^{18}O$) are reported with respect to SMOW, and $\delta^{13}C$ of the $CO_2$ gas evolved with respect to V-PDB standard. We also report oxygen isotope SIMS (secondary ion mass spectrometer or ion microprobe) analyses coupled with SEM images of petrographically unusual carbonate phases in the meteorite, which provide a link between ion microprobe data, petrographic relationships, and the multiisotopic high-precision bulk analyses, allowing placement of further constraints on the alteration history of the meteorite.

## Significance

**Martian meteorite ALH 84001 serves as a witness plate to the history of the Martian climate ∼4 Ga ago. This study describes ion microprobe $\delta^{18}O$ analyses coupled with $\delta^{13}C$, $\delta^{18}O$, and $\Delta^{17}O$ analyses from stepped acid dissolution of the meteorite that identifies a new carbonate phase with distinct isotope compositions. These new measurements of the oxygen isotope composition of carbonates within this meteorite reveal several episodes of aqueous activity that were strongly influenced by atmospheric chemistry. When paired with carbon isotope measurements, these data suggest that the ancient atmosphere of Mars was significantly depleted in $^{13}C$ compared to the present day. This implies substantial enrichment in the $\delta^{13}C$ of the atmosphere since the Noachian which may have occurred through extensive atmospheric loss.**

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## Results

Carbonates in ALH 84001 samples exhibit two striking features: both the Ca-rich and Fe-rich phases are highly enriched in $\delta^{13}C$, and the magnitude of the oxygen isotope anomaly ($\Delta^{17}O = 0.7$ ‰) is identical in both phases (Fig. 1). The sequential acid extraction technique and ion microprobe analyses of ALH 84001 reveal the presence of distinct carbonate populations of different chemical and isotopic compositions (Fig. 2 and Table 1). The first set of measurements using the acid extraction technique on ALH84001B indicated a significant difference in C and O-triple isotopes of $CO_2$ released after 12 h at 25 °C ($\delta^{13}C = 12$‰, $\Delta^{17}O = 0.3$‰) and $CO_2$ released after 3 h at 150 °C ($\delta^{13}C = 38$‰, $\Delta^{17}O = 0.6$‰). These results suggest a potential mixture between terrestrial and Martian phases; therefore, a 1-h acid dissolution step at 25 °C was performed similar to that in ref. 20 on a larger sample of the meteorite (2.012 g; ALH84001C) to remove traces of terrestrial contamination (0.0079% $CO_3$ by mass) that may have formed during its residence in Antarctica (~13,000 y; *SI Appendix, SI Discussion*). The fraction of $CO_2$ released from this 1-h reaction showed a $\Delta^{17}O = 0.03 \pm 0.06$‰ that is indistinguishable from other terrestrial/marine carbonates (20). A further 12-h dissolution step at 25 °C for sample ALH84001C (0.01% $CO_3$) revealed a chemically and isotopically distinct carbonate phase that possessed a $\Delta^{17}O = 0.73 \pm 0.05$‰ similar to the $\Delta^{17}O$ values of the Mg- and Fe-rich carbonates that dissolve at higher temperatures ($\Delta^{17}O = 0.75 \pm 0.05$‰). Because this phase was dissolved after 12 h at only 25 °C, it is certainly dominated by Ca-rich carbonate (21), which possesses a distinct $\delta^{13}C = 20$‰ and $\delta^{18}O = 25$‰ (Fig. 1). The 3-h acid extraction step at 150 °C yielded $CO_2$ with $\delta^{13}C = 38$‰ and $\delta^{18}O = 21$‰, similar to what has been previously reported for the Fe- and Mg-rich carbonate rosettes (9, 22) (Fig. 1).

A highly Ca-rich carbonate phase was also identified in thin section, and ion microprobe measurements revealed a distinct $\delta^{18}O$ enrichment that can be linked to the stepped acid extraction results (Fig. 2 and Table 1). In thin section, these Ca-rich carbonates occur as isolated domains interstitial to both silica glass and a Mg-rich carbonate matrix (Fig. 2*B*). Neither of these carbonate occurrences exhibits typical rosette morphology. The Mg-rich matrix is found adjacent to carbonate slabs, with a similar compositional range to the classic rosettes, but with an extended zone of Ca-rich carbonates (Fig. 2*B*). Corrigan and Harvey (23) suggested that these Mg-rich and Ca-rich carbonates postdate formation of the carbonate slabs and rosettes, based on petrographic data. In their proposed sequence of events, the slab carbonates formed first, followed by shock events that resulted in limited carbonate decomposition. Subsequently, the Mg-rich and Ca-rich carbonates formed in a distinct aqueous alteration event.

## Discussion

The combination of high-precision multiisotope analyses, petrographic interpretation, and ion microprobe analyses suggest that the Ca-rich phase measured in the 12-h dissolution of ALH84001C is part of the same population as the Ca-rich phase identified in thin section (23) and likely formed on Mars. Chemically, these carbonates are the most Ca-rich of the ALH 84001 carbonates measured by ion microprobe (Fig. 2*A*). Fe and Mg carbonates are not typically reactive at 25 °C (21); therefore, Ca-rich carbonate is expected to be the main product of a 12-h acid dissolution step (*SI Appendix, SI Methods*) (21). However, the stepped extraction technique does not totally separate each phase; therefore, we expect there is some minimal mixing with less reactive, more Mg-rich phases. Nevertheless, the oxygen isotopic difference between the SIMS and dual-inlet isotope ratio mass spectrometer (IRMS) measurements of the Ca-rich phase is within the variability observed in the previous ion probe measurements of the meteorite for a particular carbonate composition (~10‰), but

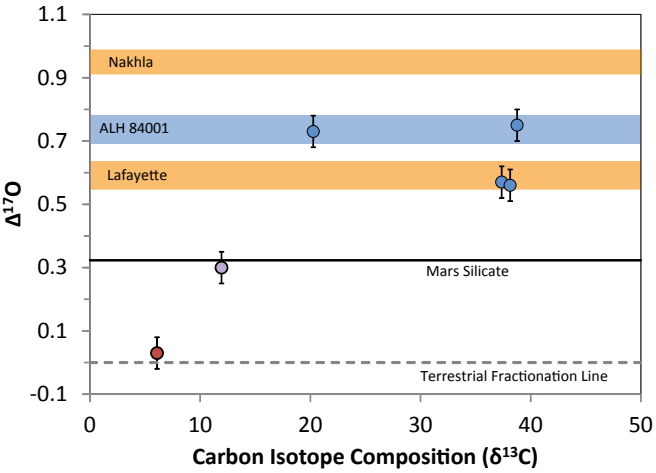


**Fig. 1.** Multi C(VPDB)-O(SMOW) triple-isotope analysis of multiple phases of carbonates in Martian meteorite ALH 84001. Blue points are analyses from this study that are interpreted to be Martian on the basis of their high $\Delta^{17}O$ values. The red point is the terrestrial contamination from the 1-h acid extraction at 25 °C. The purple point is from a 12-h extraction at 25 °C that was not preceded by a 1-h extraction, and thus this is likely a mixture between terrestrial contamination and Martian Ca-rich carbonate (Table 1). The O-isotope anomaly ($\Delta^{17}O$) of earlier carbonate measurements on Nakhlites and ALH 84001 Martian meteorites is also shown (26). However, carbon isotopic composition was not measured in these samples, and therefore these data are shown as horizontal lines. The average bulk silicate of Mars and Earth is also shown for reference.

clearly distinguishes this particular Ca-rich phase (with higher $\delta^{18}O$) from all other Ca-rich carbonates in the meteorite (Fig. 2*A*).

Multiple ion microprobe studies of the more common carbonate rosettes have shown a strong positive correlation between Mg content and $\delta^{18}O$ (7, 8, 24, 25), with all the Ca-rich phases having $\delta^{18}O$ values below 10‰ (Fig. 2*A*). The Ca-rich carbonate phase identified in the 12-h dissolution of sample ALH84001C and in the ion microprobe analyses (Table 1) does not obey this relationship, indicating formation from an aqueous event distinct from the event that formed the much more common carbonate rosettes, and thus represents a carbonate phase that has not been documented before to our knowledge. The carbon isotope composition ($\delta^{13}C = 20$‰) of the Ca-rich phase identified here also differs from the average composition of the Fe-Mg carbonate rosettes ($\delta^{13}C = 38$‰) measured during this study and previous studies (6, 9), although it is closer to some of the lowest $\delta^{13}C$ values measured by ion microprobe (Fig. 3) (6). The combined carbon and oxygen isotope data show that our stepped acid extraction technique was successful in separating a distinct carbonate phase from the more common rosettes (Fig. 3). If the $CO_2$ obtained after 12 h acid extraction of sample ALH84001C was derived from a mixture of the Fe- and Mg-rich carbonate rosettes and some other phase, it would lie on the end of a straight line drawn through the red points in Fig. 3. This would have an even lower $\delta^{13}C$ composition and higher $\delta^{18}O$ values, making it even more distinctive from the rosettes.

The significant difference in $\Delta^{17}O$ composition between terrestrial ($\Delta^{17}O \sim 0$‰) and Martian carbonates observed in this study ($\Delta^{17}O \sim 0.7$‰), along with the $\delta^{13}C$, shows the use of multiple-isotope analysis for distinguishing carbonate formed on Mars and Earth and defining processes that led to their formation (Fig. 1). Despite evidence that this $CaCO_3$ phase is distinct from the other carbonates in ALH 84001, it contains an identical $\Delta^{17}O$ anomaly (within error) to that observed in the more common Fe- and Mg-rich carbonate rosettes (Fig. 1). The O-isotopic anomaly in carbonate ($\Delta^{17}O = 0.7$‰) is higher

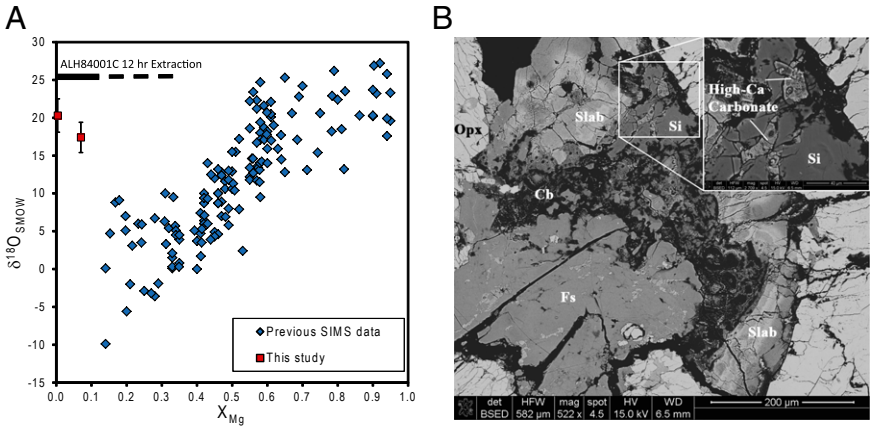


**Fig. 2.** (*A*) Blue points show relationship between the Mg content of carbonates in ALH 84001 and $\delta^{18}O$ composition from the collection of published ion microprobe analyses from ALH 84001 carbonates (7, 8, 24, 25, 35). Red points show ion microprobe analyses of Ca-rich carbonate identified in this study. These are the most Ca-rich carbonates ever studied by ion microprobe in ALH 84001 and are much more enriched in $\delta^{18}O$ than other Ca-rich phases. The black line indicates our best guess at where the 12-h extraction at 25 °C of ALH84001C would plot for comparison with the SIMS data. (*B*) Carbonate assemblage from ALH 84001,302, shown in a backscattered electron image (taken on the FEI NOVA NanoSEM 600 at the Smithsonian Institution). High-Ca carbonates analyzed for oxygen isotopes are shown in the enlargement in the upper right corner of *B*. Ovate features within carbonates are ion microprobe pits. Slab, slab-type carbonates described in Corrigan and Harvey (23); Fs, feldspathic glass; Cb, mixed carbonate (mostly magnesite); Opx, orthopyroxene.

compared with the isotopic composition of the silicate ($\Delta^{17}O$ = 0.36‰) measured on the same slice of ALH84001C, using $CO_2$ laser fluorination (26) (*SI Appendix*, Figs. S1 and S2). The higher O-isotope anomaly in the ALH 84001 carbonate compared with host rock ($\Delta^{17}O$= 0.4‰) (Table 1) is likely a result of the interaction of an anomalous fluid with the anomalous atmospheric $CO_2$ that derived its signal from the atmospheric $CO_2$-$O(^1D)$ cycle and, ultimately, ozone, the source of the O-isotope anomaly (19, 26) (*SI Appendix, SI Discussion*). Comparison of the O-triple isotope composition of carbonates from ALH 84001 with other carbonates in Nakhla and Lafayette show a similar O-triple isotopic composition that is significantly different from the host silicates (26). The present findings are also similar to other measurements of secondary minerals in Martian meteorites (SNC $\Delta^{17}O_{carbonates}$ = 0.6–0.9‰ and $\Delta^{17}O_{silicates}$ = 0.2–0.4‰) (26), which contain sulfates and water with higher $\Delta^{17}O$ anomalies compared with the host silicate rock (*SI Appendix*, Fig. S1*B*). NWA7034 provides an exception to this trend, where $\Delta^{17}O_{silicates}$ = 0.6‰ of the host rock is higher than that of the secondary minerals $\Delta^{17}O_{carbonates}$ = 0‰ and $\Delta^{17}O_{sulfate}$ = 0‰ for presently unknown reasons (20). If the carbonates precipitated from liquid water, it is likely that the ancient water reservoir on Mars possessed a significant oxygen isotope anomaly.

The isotopic composition of the Ca-rich phase measured in this study indicates that the Ca-rich phase is likely distinct from the more common carbonate rosettes. However, they may still have formed from the same carbon reservoir, despite having a different oxygen isotope composition (Fig. 3). Petrographic relationships show that the Ca-rich phase postdates the more abundant Mg- and Fe-rich rosettes and formed in a distinct alteration event (5, 23, 27). The absolute timing of this later alteration event is difficult to constrain and may represent either an event that occurred soon after the primary population of carbonate rosettes formed (~3.9 Ga) or an even later event, perhaps the one that ejected the meteorite from Mars (~15 Ma) (28). Recrystallization of carbonate during/after impact (12, 29)

**Table 1. C and O-triple isotope data of carbonate extracted from ALH 84001, using step-wise acid etching technique and ion microprobe (SIMS) analyses**

| Sample | Treatment | % $CO_3$ by mass | $CO_2$ µmole | $O_2$ µmole | $\delta^{13}C$ | $\delta^{17}O'$* | $\delta^{18}O'$* | $\Delta^{17}O$ |
|---|---|---|---|---|---|---|---|---|
| ALH84001C | 1 h at 25 °C | 0.0079 | 2.69 | 2.58 | 6.09 | 19.16 | 36.51 | 0.03 |
| ALH84001C** | 12 h at 25 °C | 0.01 | 3.45 | 3.36 | 20.27 | 14.14 | 25.60 | 0.73 |
| ALH84001C† | 3 h at 150 °C | 0.145 | 14.56 | 13.8 | 38.77 | 11.99 | 21.46 | 0.75 |
| ALH84001C‡ | Laser fluorination | | | | | 2.54 | 4.17 | 0.36 |
| ALH84001A | 3 h at 150 °C | 0.13 | 6.08 | 5.15 | 37.37 | 12.59 | 22.93 | 0.57 |
| ALH84001B** | 12 h at 25 °C | 0.014 | 0.735 | 0.65 | 11.94 | 18.33 | 34.42 | 0.30 |
| ALH84001B† | 3 h at 150 °C | 0.12 | 6.09 | 4.15 | 38.14 | 12.17 | 22.16 | 0.56 |
| ALH_302_9 | SIMS | — | — | — | — | — | 17.4 ± 2.0 | — |
| ALH_302_15 | SIMS | — | — | — | — | — | 20.3 ± 2.2 | — |

Three different extractions were performed, labeled ALH84001A, ALH84001B, and ALH84001C. Sample A did not contain sufficient $CO_2$ after 12 h at 25 °C, and the 1-h extraction was not performed. The 1-h extraction was also not performed for sample B, but sufficient sample was recovered at the 12-h time step. The overall uncertainty for the complete procedure ($CO_2$ acid extraction, gas chromatography, fluorination, and isotope analysis), based on repeated samples similar in size and composition to the Martian rock samples, is ±0.1‰ for $\delta^{13}C$ and ±0.2‰ for $^{17}O$ and $^{18}O$. Statistical variations (1σ SD) using laboratory $CO_2$ standards on IRMS were $\delta^{13}C$ = ±0.02‰, $\delta^{17}O$, and $\delta^{18}O$ = ±0.1‰. Chemical composition of SIMS spots were measured by Eprobe (*SI Appendix, SI Methods*): ALH_302_9, $Ca_{90}Mg_7Fe_3$; ALH_302_15, $Ca_{99}Mg_0Fe_1$.

*$\delta^{i}O' = 1000 \ln(1 + \delta^{i}O/1000)$ where $^{i}O$ = $^{17}O$ and $^{18}O$.

**25 °C acid dissolution, which mostly releases $CO_2$ from the Ca-rich phase.

†150 °C acid dissolution, which releases $CO_2$ from the Fe-Mg-Mn-rich phase.

‡O-triple isotopic composition of the whole rock, using laser fluorination (26).

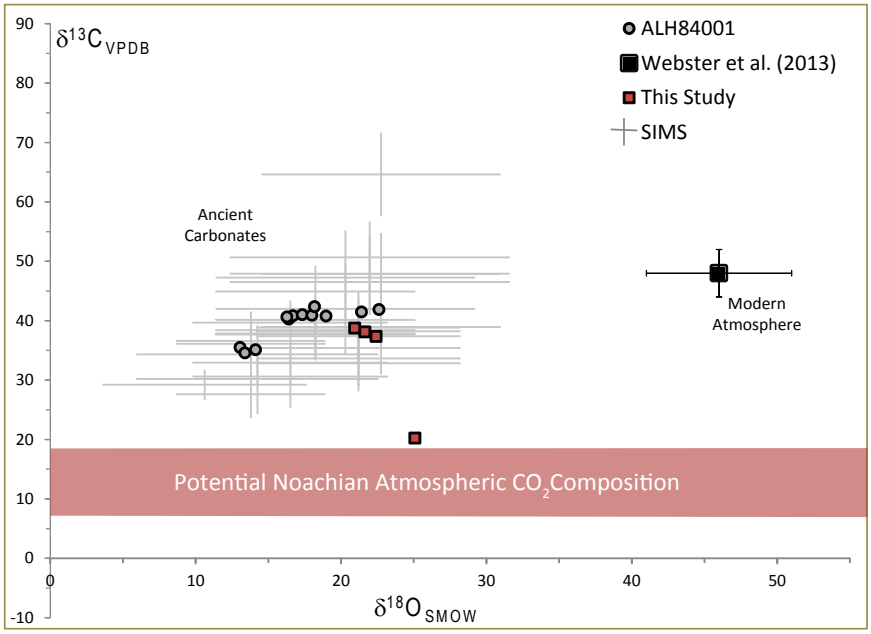


**Fig. 3.** Data from this study and other stepped dissolution measurements of ALH 84001 showing the variation in $\delta^{13}C$ observed in this study for Martian phases (9, 22). Gray crosses indicate the range of values from SIMS studies correlated by Mg contents. Red points are from acid dissolution measurements conducted in this study. The $CaCO_3$ phase is distinct from the covariant trend in other ALH 84001 carbonates, indicating that it formed from a distinct aqueous event. However, the covariant trend indicated by the rest of the ALH 84001 data potentially points to an initial atmospheric composition near 15‰, which would also be consistent with the Ca-rich carbonates measured in this study.

would allow it to preserve its interaction with the modern atmospheric $CO_2$ through a transition stage at higher temperature, as suggested in previous studies, following the reaction sequence outlined in Fig. 4. This scheme involves replacement of all C and two-thirds of the O atoms in carbonates with modern atmospheric $CO_2$ during the recrystallization process (30). Because of the large sample required for geochronological dating, only petrographic and C-O triple isotope compositions are available to interpret the origin of the Ca-rich phase that constitutes a minor component of the rock (~0.01%). The textural and isotopic analysis suggest that the Ca-rich phase postdates the Mg-rich phase, based on the presence of the Ca-rich phase in the cataclastic zones and a ~18‰ shift in $\delta^{13}C$.

The carbon isotope geochemistry of the carbonates in ALH 84001 is complex and remains difficult to interpret with only two isotopes. In particular, it would be useful to be able to constrain the carbon isotope composition of the Martian atmosphere ~3.9 Gya, using the carbonates preserved in this meteorite. As discussed, the $\Delta^{17}O$ composition of these carbonates suggests a strong influence of an atmospheric component, and the similarity in $\Delta^{17}O$ between the Ca-rich phase and the more common rosettes suggests a close relationship. The variation in $\delta^{13}C$ is very large, with the results from this study extending it even farther. Niles and colleagues (6) reported a range of $\delta^{13}C$ values between 28‰ and 64‰, with the most Ca-rich phases having the lowest $\delta^{13}C$ values. This study extends that range down to 20‰, probably by sampling a much more Ca-rich phase. Lower $\delta^{13}C$ values than this have been reported as well, although the amount of terrestrial contamination in these analyses is not clear (31, 32).

Overall, the carbon isotopic composition of the Ca-rich phase agrees with the trend of lower $\delta^{13}C$ with lower Mg content found in previous work (6). The problem is that the $\delta^{18}O$ composition is much higher than would be expected for the Ca-rich composition of the carbonate and is completely out of the field of previous analyses (Figs. 2*A* and 3). If the Ca-rich phase measured here formed as part of the aqueous event that formed the rest of the ALH 84001 carbonates, it has some interesting implications for different models of carbonate formation that have been proposed.

Several different ALH 84001 carbonate formation models for the slabs/rosettes have implications for the ancient Martian environment. If this Ca-rich phase formed in close association with the slab/rosettes, then these models are tested. However, if the Ca-rich phase formed in a separate aqueous event altogether, then different conclusions apply (see following). For example, it has been proposed that the carbonate slab/rosettes formed from a high-pH fluid (6) that initially contained no $CO_2$ and rapidly precipitated carbonates on exposure to a $CO_2$-rich atmosphere. In this case, there is a strong kinetic fractionation favoring the light isotopes, resulting in carbonates depleted in $\delta^{13}C$ compared with the atmosphere. According to this model, the ancient atmosphere would have to have had a $\delta^{13}C$ value between 30‰ and 40‰, and the $\delta^{18}O$ covaries with the carbon as a result of the inclusion of $OH^-$ (depleted in $\delta^{18}O$) during initial carbonate formation. Thus, assuming the Ca-rich phase formed under similar conditions as the slab/rosettes, it would be very difficult to obtain a carbonate with low $\delta^{13}C$ and high $\delta^{18}O$ under these conditions, as both isotope compositions are pH-dependent and covary. Although the rosettes may have formed via this mechanism, there is no clear way to explain the existence of the Ca-rich phase, which has a relatively low $\delta^{13}C$ and high $\delta^{18}O$, without major changes to the atmospheric $\delta^{13}C$.

Other models have been based on observations of other Ca-rich carbonates with relatively low $\delta^{18}O$ (25) in the meteorite.

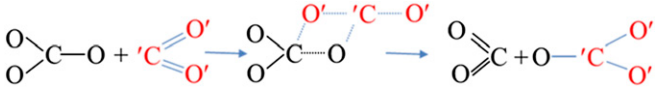

**Fig. 4.** Schematic showing interaction of ancient carbonates with modern $CO_2$ via transition state and recrystallization of carbonates. Red letters with prime symbol indicate modern $CO_2$; dotted line indicates formation of new bonds during the transition stage of recarbonation.

These studies have suggested that the Ca-rich carbonates formed from high-temperature hydrothermal fluids (13) that possessed lower $\delta^{13}C$ and $\delta^{18}O$ as a result of interaction with silicates and magmatic reservoirs. If the Ca-rich hydrothermal fluid was indeed a product of subsurface hydrothermal interaction, it should possess a $\Delta^{17}O$ similar to the silicates, instead of a $\Delta^{17}O$ anomaly derived from extensive atmospheric interactions. The Ca-rich phases identified in this study have a higher $\delta^{18}O$ composition, indicating a likely low-temperature origin, and they also have a large $\Delta^{17}O$ anomaly, indicating they did not likely form from hydrothermal fluids. However, it remains possible that the $\delta^{18}O$-poor, Ca-rich carbonates observed in ref. 25 do not have an oxygen isotope anomaly, and were therefore formed from hydrothermal fluids. A clear measurement of the $\Delta^{17}O$ in the $\delta^{18}O$-poor, Ca-rich cores of the slab/rosettes has not been performed and is needed to evaluate this model better.

Finally, it has also been suggested that the carbonates formed from a single $CO_2$-rich fluid that began degassing and evaporating as it was exposed near the surface (22, 33). This would suggest an ancient atmosphere that possessed a $\delta^{13}C$ of 15–20‰, whereas the carbonates obtained their heavier and covariant carbon and oxygen isotopic compositions through Rayleigh distillation effects during evaporation and degassing. This provides a compelling model to understand the slab/rosettes, and if the Ca-rich phase identified in this study formed under similar conditions, it may have formed from the fluid after the initially $CO_2$-rich fluid had degassed, evaporated, and precipitated the bulk of the carbonates. The resulting fluid could have then reequilibrated with the atmosphere, lowering the $\delta^{13}C$ back to its starting levels (~20‰). In this case, the $\delta^{18}O$ would remain elevated because the fluid had been enriched by evaporation, and the oxygen would not have been affected by the $CO_2$ reequilibration because of mass balance. The main drawback to this model is that the evaporated fluid should be Mg-rich because the Mg carbonates are much more soluble than the Ca-rich carbonates. It is difficult to explain how the carbonates might become Ca-rich again, as the evaporation process should have depleted the fluid in $Ca^{2+}$.

All of the previous discussion has assumed that the Ca-rich phase measured in this study formed in close relation to the other carbonates in the meteorite, and therefore could be understood in their context. It is certainly possible that this is not the case, and that the Ca-rich phase observed here formed in a completely unrelated event that substantially postdated the formation of the bulk of the carbonate within the rock. In this case, the variation in the oxygen isotopic composition could be understood as being a result of a different aqueous fluid with different $\delta^{18}O$ composition. This is quite possible, as $\delta^{18}O$ variations can be caused by different precipitation patterns, changes in water source, or any number of other things. The $\delta^{13}C$ of the Ca-rich phase may just represent the composition of the atmosphere at the time of formation, especially as the $\Delta^{17}O$ content indicates a close atmospheric relationship. If the Ca-rich phase precipitated at room temperature similar to the rosettes (22), it suggests that the atmosphere $\delta^{13}C$ was near 13‰. This atmospheric composition is very similar to what is predicted by the degassing/evaporation models (22, 33) outlined in the case where the Ca-rich carbonate formed in close association with the slab/rosettes, presented earlier (Fig. 3).

Importantly, it does not matter whether the Ca-rich phase formed in association with the slab/rosettes or not. In both cases, the most feasible models predict a $\delta^{13}C$ value of the ancient atmosphere that is between 10‰ and 20‰. This $\delta^{13}C$ value for the ancient atmosphere is significantly different from the $\delta^{13}C$ of the modern atmosphere recently measured by the Mars Science Laboratory (46‰) (34). There is a distinct possibility, given our lack of knowledge of the oxygen budget on Mars, that the Ca-rich phase does not record the atmospheric composition, despite possessing a $\Delta^{17}O$ anomaly. However, given the strong atmospheric signature recorded in this phase and its similarity to the other carbonates in the meteorite, it suggests that the carbon isotope composition of the Noachian atmosphere had a substantially lower $\delta^{13}C$ value at 4 Ga. This implies substantial enrichment in the $\delta^{13}C$ of the atmosphere since 4 Ga, which may have occurred through extensive atmospheric loss.

## Methods

Martian rock ALH 84001–214 was treated with concentrated phosphoric acid, and $CO_2$ extracted was used to measure C and O-triple isotopes (*SI Appendix, SI Methods*). Ion microprobe oxygen isotope measurements were obtained from two separate thin sections of ALH 84001 (302 and 303), using the CAMECA ims 6f at Arizona State University and the CAMECA ims 1270 at the University of California, Los Angeles. Samples and standards were coated with ~20–30 nm of carbon (*SI Appendix, SI Methods*).

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